

## Advanced Materials and Multifunctional Structures for Aerospace Vehicles

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### ABSTRACT

*This paper presents a critical review of the work on Advanced Materials for Multi Functional Structures in Aerospace Vehicles. The advanced synthesis, processing and the characterization techniques that facilitate the design of multifunctional aerospace materials leading to their reliable and high performance in extreme environments will be reviewed. The focus areas of this paper will be materials for sensing, actuation and damping, damage tolerant and adaptive structures, anti-icing and multifunctional coatings. Other properties considered for design are electrical conductivity, thermal resistance, radiation shielding and resistance to impact loading.*

*Multifunctional materials also offer numerous possibilities for the development of components and devices that are lighter, stronger, stiffer, and more resistant to extreme environments in aerospace applications. The nano-layered and nano-composite coatings developed in recent years are now not only able to sense corrosion and mechanical damage to the aircraft skins, but they are also able to sense chemical and physical damage, promote adhesion and fatigue resistance and also offer self-cleaning possibilities.*

### 1.0 INTRODUCTION

Materials are said to be multifunctional when more than one primary function is performed either simultaneously or sequentially in time. These systems are based on metallic, ceramic and polymeric materials, the framework for which is based on materials science, mathematics and engineering physics. These materials systems with structural capabilities may be fully integrated with sensing, actuation and in some cases with healing capability. The attainment of multifunctionality has been achieved by controlling properties at the nano, micro and macro scale. In this paper, properties of a variety of materials will be reviewed with particular emphasis on potential applications in the aerospace sector.

### 2.0 ADAPTIVE SYSTEMS

Adaptive systems, based on shape memory alloys (SMAs) and piezoelectric materials have attracted much attention recently. The martensitic phase transformations in the SMAs are accompanied by significant changes in physical and mechanical properties, such as hardness, yield strength, Young's modulus, thermal expansion

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coefficient, thermal conductivity, damping, etc, making them adaptable to the external changes in temperature, stress, electrical or magnetic field<sup>1</sup>, as shown in Table 1. The piezoelectrics have been demonstrated to be effective active materials in many transducers and controlled structures applications. The high stiffness of piezoelectrics gives them high actuation authority, and piezoceramics are easily controlled through an applied voltage. Moreover, the high bandwidth of piezoelectrics makes a large range of applications possible<sup>2</sup>.

**Table 1: Some typical properties of binary Ti-Ni shape memory alloys<sup>1</sup>**

melting point, K	~ 1573	
density, g cm <sup>-3</sup>	6.4-6.5	
transformation temperatures, K	173-390	
transformation enthalpy, kJ mol <sup>-1</sup>	1.46-1.88	
transformation hysteresis	20-50	
recoverable strain, %	< 8 (one-way), < 5% (two-way)	
recoverable stress, MPa	< 500	
damping capacity, Q <sup>-1</sup>	~ 10 <sup>-2</sup>	
ultimate tensile strength, MPa	800-1100	
	parent phase	martensite
yield strength, MPa	200-800	70-200
young's modulus, GPa	50-90	10-35
shear modulus, GPa	15-20	3.5-5
thermal expansion coefficient, ×10 <sup>-6</sup> K <sup>-1</sup>	10.0-11.0	5.8-8.6
thermal conductivity, W cm <sup>-1</sup> K <sup>-1</sup>	0.18	0.086
electrical resistivity, μΩ cm	70-110	40-70
magnetic susceptibility, ×10 <sup>-6</sup> e.m.u.g <sup>-1</sup>	2.7-3.0	1.9-2.1

Although the SMAs and piezoelectrics can be used alone as adaptive systems, the use of SMA bulk materials suffers from the high density and slow response, as the SMAs are usually heat actuated and the heat must be removed between actuation cycles; meanwhile, the piezoelectrics are very brittle, giving rise to difficulties in manufacturing and application of large scale piezoelectric components. Therefore, adaptive composites based on SMAs and piezoelectrics, as oppose to bulk SMAs and piezoelectrics, are more promising candidates for applications in aircraft structures.

### 2.1 Adaptive Systems Based on SMAs

Three distinct configurations of SMA wires for control of frequency and shape of a structure are:

- Embedded in composite structures
- Connecting externally to the structure
- Inserting in composite structure via sleeves<sup>3</sup>.

Structural tuning, vibration and acoustic control can be accomplished through the change of stiffness of the embedded SMA fibers<sup>4</sup>, which is known as active property tuning (APT), or activating the pre-strained SMA fibers to generate a stress that will tailor the structural performance and modify the modal response of the whole composite system<sup>5,6</sup>, known as active strain energy tuning (ASET). In general, a large volume fraction of SMA fibers without prior plastic deformation is required for APT, which will not create any large internal

stresses, whereas a significantly reduced amount of pre-strained SMA fibers will be necessary for ASET and, at the same time, will generate large internal stresses throughout the structure<sup>6</sup>.

Studies have shown that utilizing polymer matrix composites to replace the conventional aluminum tail rotor drive shaft of helicopters would lead to significant weight savings<sup>7,8</sup>; however, an external damper would be needed for such a composite shaft to reduce its response under resonance condition<sup>9</sup>. The need for an external damper can be avoided through the use of SMA actuators to alter the natural frequencies of the shaft. The resonance frequencies of SMA embedded composites usually increase when the SMA wires are activated, as shown in Figure 1, and the increment of resonance frequencies increases with increased volume fraction of SMA wires<sup>3,10</sup>. However, a decrease in resonance frequencies was also observed, when the volume fraction of SMA wires was very small<sup>11</sup>. When properly trained, SMA wires act as linear actuators and can be activated to alter the shape of the airfoil, increasing the efficiency of a wing in flight<sup>12</sup>. Moreover, the development of high temperature shape memory alloys (HTSMA), such as Cu-Al-Ni single crystals, may provide controllable actuation of aircraft control surfaces during flight or deployment of actuators in/near engines or power trains, etc<sup>13</sup>.

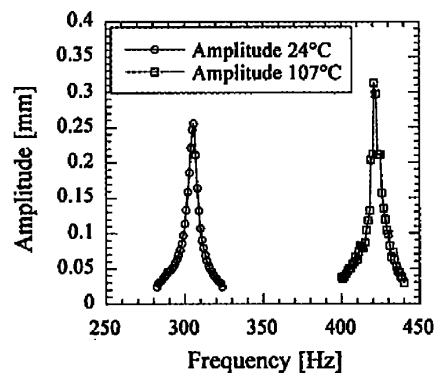


Figure 1: Resonance peak shift as SMA wires activated<sup>10</sup>.

While the martensitic transformation underlying the shape memory effect plays a very important role in SMA embedded composites, the use of R-phase transformation<sup>14,15</sup> can be more favourable for on-off control of adaptive composites, thanks to the small hysteresis associated with this transformation and the small temperature and strain window<sup>16</sup>. The R-phase transformation shows unique characteristics, making it more appropriate for the actuation of SMA embedded composites in many cases<sup>17</sup>. Also, the maximum transformation strain associated with the R-phase transformation is very small, resulting in lower shear stress at the SMA wire-polymer matrix interface, leading to excellent cyclic stability<sup>18</sup>.

SMA thin films, on the other hand, are considered excellent candidates for micro-electro-mechanical systems (MEMS), due to their desirable mechanical properties, such as their ability to exert a stress of hundreds of megapascals, their ability to tolerate strains of more than 3% common Transistor-Transistor Logic (TTL) voltages, and their ability to survive millions of cycles<sup>19,20,21,22,23</sup>. The SMA thin films are usually deposited onto silicon substrates<sup>22,23,24,25,26</sup>, and such systems can be used in micro-devices such as micro-valves and micro-actuators<sup>19,20,27,28</sup>.

## 2.2 Adaptive Systems Based on Piezoelectrics

Lead zirconate titanate (PZT) piezoelectric ceramics have also been used as actuators for vibration control and electronic damping<sup>29,30,31</sup>. When piezoceramic actuator embedded epoxy matrix composite is integrated into a rotor blade, it may suppress rotor vibration<sup>32</sup> by twisting the blade to vary the angle-of-attack to introduce aerodynamic loads, and thus increase the helicopter payload and cruise speed<sup>33</sup>. In order to develop piezoelectric actuators as elements of intelligent structures, monolithic piezoceramic wafers are individually embedded in composites, which consequently reduce the strength of the composites<sup>34</sup>; however, the active members should be able to withstand repeated tensile mechanical loads at a low strain level<sup>35</sup>. In this configuration, embedded actuators have to be individually insulated from the conducting graphite and each wafer must have a separate electrode leading to the composite perimeter, which requires an unacceptable number of electrode leads within the composite substrate for large scale applications<sup>36</sup>.

Other attempts to embed piezoceramics in blade structures have been made. In an early work, piezoelectric elements were embedded under the fiberglass skin in banks of discrete actuators on the top and bottom surfaces of the blade, which produced both twist distribution and bending distribution along the blade<sup>32</sup>; however, the magnitude of blade twist obtained was small<sup>32,37</sup>.

Continuous piezoelectric fiber composite (PFC) was introduced<sup>38</sup>, as an alternative to monolithic piezoceramic wafers, and was embedded in laminated graphite/epoxy host structures for actuation applications<sup>39</sup>. The PFCs, coupled with interdigitated electrodes (IDEs)<sup>40</sup>, are chosen for their suitability for embedding in composite laminates, high actuation, and robustness provided by the composite fiber/epoxy configuration<sup>41</sup>. This interdigitated electrode piezoelectric fiber composite (IDE-PFC) system (Fig. 2a), also known as active fiber composite (AFC), provides an anisotropic actuation<sup>42</sup>. When two AFC actuators are configured as 45<sub>A</sub>/0<sub>S</sub>/45<sub>A</sub> antisymmetric angle-ply laminate (Fig. 2b), it will demonstrate twist actuation by introducing a shear deformation. Extensive evaluations were conducted to determine the mechanical properties, mechanical fatigue behaviour, electro-mechanical coupling properties and electrical fatigue properties<sup>43,44,45,46</sup>. A prototype blade, embedded with AFC actuators, was manufactured and tested successfully in both bench and hover conditions<sup>47</sup>, and the AFC-actuator embedded blade demonstrated a dynamic blade twist in wind tunnel testing<sup>48</sup>.

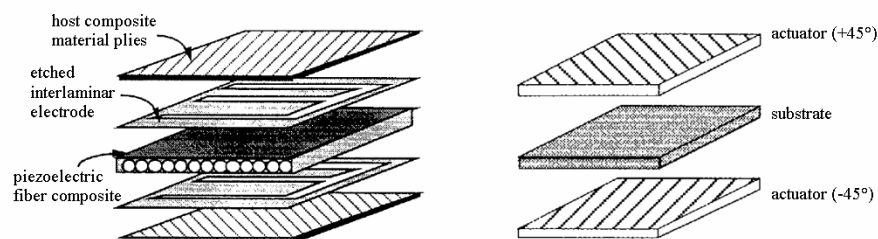


Figure 2: Piezoelectric fiber composites (a) and twist-extension coupled laminate (b)<sup>42</sup>.

## 2.3 Electro-Active Polymer Materials

Electroactive polymers (EAPs) are an emerging class of actuation materials. Their large electrically induced strains (longitudinal or bending), low density, mechanical flexibility, and ease of processing offer advantages over traditional electro-active materials<sup>49</sup>. EAPs can be identified as electronic EAPs, such as electro-strictive

polymers, and ionic EAPs such as conductive polymers and ion-exchange polymer metal composites (IPMCs).

Electro-strictive polymers usually exhibit high and fast response within an electric field with high voltages, along with relatively large induced actuation forces. Also, the strain achieved by the electric field is nominally proportional to the square of the applied electric field<sup>50,51,52,53,54,55</sup>. However, actuators based on electro-strictive polymers require high voltages to operate, leading to integration problems at the system level<sup>56</sup>. A study showed that the operating voltage to stimulate the actuator could be reduced when doping fullerene into an electrostrictive polymer<sup>57</sup>.

Ionic EAPs usually contain an electrolyte and respond to an external electric field as a result of the movement of ionic species within the polymer network. The actuation of conductive polymer based devices is based on dimensional changes due to the volume required to accommodate dopant species, anions or cations, within the polymer network<sup>58</sup>. The electrically generated strain of a conductive polymer actuator is mainly controlled by the charge transferred between anode and cathode; depend on the applied voltage and not the applied electric field. The IPMC actuators are made of an ion conducting membrane material incorporated with lithium or sodium, which is plated with metal electrodes, such as platinum<sup>59,60,61,62</sup>. While the actuation mechanism of IPMCs is similar as conductive polymers in that ion movement causes a dimensional change in the material, the IPMC actuators require much lower voltage to be operated. The ionic EAPs, in general, provide a slow response and need to be moist continuously, since the performance degrades as the material becomes dry<sup>63</sup>. A polysilicon coating technique was thus developed to maintain the moisture content of the ionic EAPs, extending their operation in air from a few minutes to about four months<sup>59</sup>. Ionic EAP actuators are considered potential candidates for microflaps for aircraft wings<sup>58</sup>.

### 3.0 PROTECTIVE COATINGS

The ingestion of solid particles such as sand, salt or ice into aircraft engines results in deterioration of the compressor by impingement of particles on the blade surfaces possibly leading to structural failure of the blades<sup>64</sup>. As aircraft engines operate at high temperatures, oxidation and hot corrosion damage will also occur as a result of sea salt from the environment and sulfur in fuels, leading to deterioration of engine hot section components, including the turbine and combustor. As such, development and application of wear- and corrosion-resistant coatings for compressor components, as well as thermal- and hot corrosion-resistant environmental barrier coatings for high temperature turbine components are in high demand.

#### 3.1 Hard Coatings for Erosion, Wear and Corrosion Protection

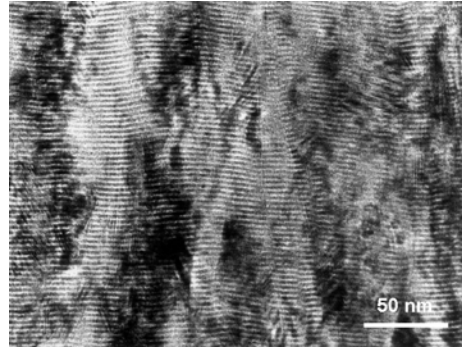
A coating that provides both erosion resistance and corrosion resistance, deposited onto aircraft compressor components such as blades and rotors, should improve the durability of the components during service, thus reducing repair cost.

Nitride based multilayered coatings, usually deposited by physical vapor deposition (PVD) techniques, have demonstrated improved durability for tribological applications. Multilayers can be divided into two categories<sup>65</sup>: isostructural multilayers contain individual layers having the same crystallographic structure, such as TiN/NbN, TiN/VN, TiAlN/ZrN and TiN/CrN; whereas non-isostructural multilayers consist of layers with different crystallographic structures, such as TiN/AlN, TiN/TaN and TiN/CN<sub>x</sub>, providing a further barrier to dislocation motion. Moreover, superlattice multilayers exhibit significant hardness enhancement<sup>66,67,68,69,70</sup>. The hardness range of most multilayered coatings is 30-60 GPa, and in general it will gradually decrease



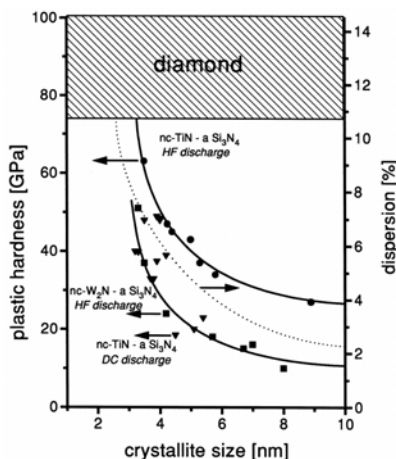
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when temperatures increase to above  $500^{\circ}\text{C}$ <sup>71,72,73</sup>. Figure 3 shows the morphology of a typical TiN/AlN superlattice multilayer coating<sup>74</sup>.

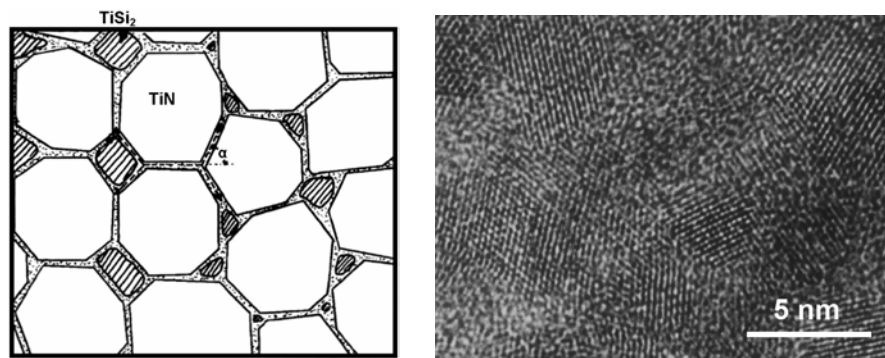


**Figure 3: Morphology of a TiN/AlN multilayer coating with growth direction from bottom to top<sup>74</sup>. The dark layers are TiN, and the bright layers are AlN. TEM bright field image.**

Another methodology to produce hard coatings for tribological applications is to deposit a layer of nanocrystalline/amorphous (nc-/a-) composite material onto the substrate, using either plasma enhanced chemical vapor deposition (PCVD) or PVD techniques<sup>75,76,77,78</sup>. For example the Ti-Si-N system, deposited by PCVD, has extremely high hardness<sup>75,79,80</sup> (Fig. 4), which is believed to result from the nc-TiN/a-Si<sub>3</sub>N<sub>4</sub>/a-TiSi<sub>2</sub> structure<sup>81,82</sup>. It was suggested that the Ti-Si-N nanocomposite microstructure consists of TiN nanocrystals covered with a monolayer a-Si<sub>3</sub>N<sub>4</sub><sup>83</sup>, as illustrated in Figure 5. Other nanocomposite coating systems, such as Ti-C<sup>84</sup>, Ti-B-C<sup>85</sup>, Ti-B-N<sup>77,85</sup>, Ti-B-C-N<sup>86,87</sup>, Ti-Al-Si-N<sup>88,89,90,91</sup>, Ti-Cr-C-N<sup>92</sup>, Ti-Si-B-N<sup>93</sup> and Ti-Si-C-N<sup>94,95,96,97</sup>, also exhibit very high hardness when the composition and deposition parameters are carefully selected. When annealed for a short period of time, Ti-B-N and Ti-Si-N remain stable up to  $800\text{--}900^{\circ}\text{C}$ <sup>77,98</sup>, Ti-Si-C-N remains stable up to about  $1000^{\circ}\text{C}$ <sup>99</sup>, while Ti-Al-Si-N is stable up to  $1000\text{--}1100^{\circ}\text{C}$ <sup>90,98</sup>. It was also shown that, in general, a harder coating is more resistant to wear<sup>78,97</sup>.



**Figure 4: Hardness of nanocomposites as a function of crystalline size<sup>80</sup>.**



**Figure 5: Schematics of the Ti-Si-N nanocomposites<sup>81</sup> (a) and microstructure of nanocrystalline Ti-Si-C-N film<sup>94</sup> (b).**

The corrosion resistance of the coatings depends on the processing method, coating composition and corrosion medium. For example, the Ti-B-N film was reported to be more corrosion resistant than TiN in 0.1 N H<sub>2</sub>SO<sub>4</sub> solution<sup>100</sup>; however, it showed poor corrosion resistance in 1 N H<sub>2</sub>SO<sub>4</sub> solution<sup>101</sup>. (Ti,Al)N coatings are less corrosion resistant than TiN in 1 N H<sub>2</sub>SO<sub>4</sub> solution, however (Ti,Al)N+AlN multilayer coatings outperform the TiN coating in the same solution<sup>101</sup>. Also, research on Ti-C-N coatings showed that increasing carbon content in the coating reduced the corrosion resistance in 1 N H<sub>2</sub>SO<sub>4</sub> solution<sup>102</sup>; nevertheless, it was shown that Ti-C based coating systems, such as Ti-C, Ti-Si-C-N, Ti-Ta-Mo-C and Ti-C-Fe-Si-Mo, have enhanced corrosion resistance in 5 N H<sub>2</sub>SO<sub>4</sub> solution, with a corrosion rate of less than 10 μm/year at room temperature<sup>103</sup>.

It has been demonstrated that, Ti-C and Ti-Si-C-N nanocomposites coatings seem to be the most promising candidates for compressor applications, owing to their high hardness<sup>84,94,95,96,97</sup>, good high temperature hardness retention<sup>99</sup>, and good corrosion resistance<sup>103</sup>. However, long term high temperature durability and corrosion resistance in salt environment need to be determined before application in aircraft engines. On the other hand, oxides that are stable in air may also be used in multilayered coatings, with either TiN or TiC, to provide both high strength and chemical inertness<sup>66</sup>.

### 3.2 Composition Gradient Coatings

For most metals and alloys, a thin oxide layer formed spontaneously at the surface in a specific environment, known as passive film, can slow corrosion reactions. Artificial passivation films that simulate the composition, crystal structure, and thickness of passive films on corrosion-resistant metals and alloys, have been produced by various processes in order to enhance corrosion resistance. As oxides are susceptible to mechanical damage, localized corrosion will occur at damaged sites. As such, corrosion resistant coatings with self-healing ability are very attractive for both civilian and military applications<sup>104,105</sup>.

Oxide/metal multilayer films, such as Al<sub>2</sub>O<sub>3</sub>/Al/Al<sub>2</sub>O<sub>3</sub>/Al and Al<sub>2</sub>O<sub>3</sub>/Nb/Al<sub>2</sub>O<sub>3</sub>/Nb<sup>106</sup>, were found to have self-healing ability; however, corrosion proceeded preferentially along the metallic layer from intrinsic pinhole defects in the films. It was found that oxide-metal nanocomposite films, such as Al<sub>2</sub>O<sub>3</sub>·Nb, exhibit excellent self-healing ability; however, increasing Nb content in such films increases pinhole density within the film. A composition-gradient Al<sub>2</sub>O<sub>3</sub>·Nb nanocomposite film, with increased Nb content from the film surface to the substrate interface, was therefore developed, with an Al<sub>2</sub>O<sub>3</sub>/composition-gradient Al<sub>2</sub>O<sub>3</sub>·Nb/Nb/substrate configuration showing the best corrosion resistance<sup>104</sup>.



### 3.3 Thermal and Environmental Barrier Coatings

The improved performance of gas turbine engines is directly related to the increase of turbine inlet temperature, as a result of improved structural design, airfoil cooling, and use of high strength-at-temperature alloys as well as protective coating systems<sup>107</sup>. Coatings that can act as a barrier to both heat and hot corrosion, will enable gas turbine engines to operate at higher temperatures and improve the durability of components, leading to improved turbine performance and reduced service cost.

ZrO<sub>2</sub>-base ceramics were considered for thermal barrier coating (TBC) applications because of their low thermal conductivities, high melting point and thermal expansion coefficients<sup>108,109,110</sup>. It was found that zirconia-(6-8 wt.%)Yttria TBCs, with a tetragonal zirconia structure formed by a diffusionless shear transformation directly from the cubic phase, are rather stable up to 1400°C<sup>111</sup>, and were considered the best when deposited on a metallic bond coat<sup>112,113</sup>. The two most popular processes to produce TBCs are thermal spray<sup>112</sup> and electron-beam physical vapor deposition (EB-PVD)<sup>114,115,116</sup>. EB-PVD produced TBCs have a columnar microstructure with a smooth interface between the ceramic coating and the metallic bond coat, while thermally sprayed TBCs have plate-like porosity across the coating<sup>117</sup>, as shown in Figure 6. Thermally sprayed TBCs generally have shorter thermal-cycling lives than EB-PVD TBCs. While thermally sprayed TBCs have served well in industrial gas turbines, because of lower operating temperatures along with reduced temperature gradients and fewer thermal cycles, EB-PVD TBCs are more durable and thus are preferred for use on turbine blades and vanes in aircraft engines, which experience much more severe operational conditions<sup>118</sup>.

The metallic bond coat, applied to the exterior surface of the component prior to ceramic deposition, is an oxidation-resistant layer and essentially dictates the spallation failure of the TBC systems. The bond coat is typically made of MCrAlY (M=Ni and/or Co), deposited by thermal spray or EB-PVD, or Pt-NiAl produced by electroplating in conjunction with diffusion-aluminizing or chemical vapor deposition (CVD)<sup>118</sup>. Table 2 shows some examples of EB-PVD TBC systems in aircraft engines. During engine operation, the formation of a thermally grown oxide (TGO) layer is the most important phenomenon responsible for the spallation failure of TBC systems. The formation and growth of an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> TGO result in the depletion of Al in the bond coat, leading to the formation of other oxides such as Ni- and Co-containing spinels, (Cr,Al)<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> in the MCrAlY bond coats<sup>119,120,121</sup>. The formation of these phases compromises the structural integrity of the TGO and accelerates localized oxidation by providing fast oxygen-diffusion paths<sup>118</sup>. On the other hand, the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer is probably the only oxide product formed in Pt-NiAl bond coat during thermal exposure<sup>122,123</sup> before TBC spallation. The addition of Pt was believed to suppress the formation of Ni-rich oxide, promote Al<sub>2</sub>O<sub>3</sub> scale formation<sup>124</sup> and improve scale adhesion<sup>125</sup>. It was suggested that the beneficial effect of platinum in promoting Al<sub>2</sub>O<sub>3</sub>-rich scale formation is partly due to its role in reducing the oxygen diffusion into the alloy<sup>125</sup>.

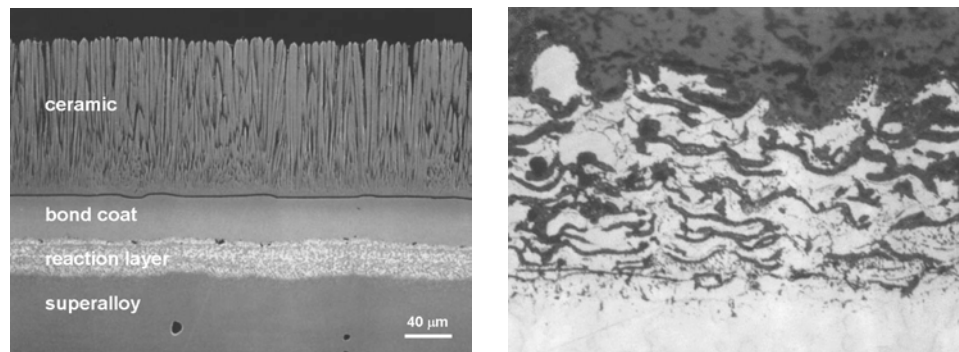


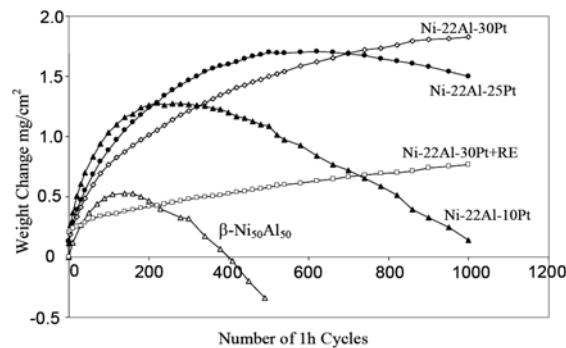
Figure 6: TBCs<sup>117</sup> produced by EB-PVD (a) and thermal spray (b).

However, the commercial  $\beta$  phase Pt-NiAl bond coat experiences a transformation from B2 to martensite and  $\gamma'$ , as a result of Al depletion from the bond coat (to the TGO and substrate) during thermal cycling, leading to bond coat expanding on heating and shrinking on cooling, thereby enhancing the strain induced by thermal expansion coefficient (CTE) mismatch<sup>126,127</sup>. A Pt-NiAl alloy with  $\gamma+\gamma'$  microstructure was developed for bond coat application in EB-PVD TBC systems, which showed a drastic improvement in oxidation resistance over the commercial  $\beta$ -Pt-NiAl at elevated temperatures<sup>125</sup>, as shown in Figure 7. In the mean time, the interdiffusion between the  $\gamma+\gamma'$  bond coat and the superalloy substrate can be significantly reduced, compared with that in the EB-PVD TBC systems with  $\beta$  Pt-NiAl bond coat. This  $\gamma+\gamma'$  Pt-NiAl bond coat is still under development<sup>128</sup>. Other developments on TBCs include high-temperature diffusion barriers between the superalloy substrate and bond coat to reduce coating degradation by lowering the rate of aluminum loss to the superalloy substrate via interdiffusion, and by inhibiting diffusion of substrate elements, such as Cr, Re, Ta and W, into the bond coat<sup>129</sup>, as well as EB-PVD TBC with reduced thermal conductivity and increased thermal reflectivity via the introduction of multilayered columnar ceramic coatings<sup>130</sup>.

Table 2: Examples for applications of EB-PVD TBC systems in aircraft engines

metallic bond coat	Pt-NiAl	MCrAlY (EB-PVD)
ceramic coating	EB-PVD	EB-PVD
GE	CF6-80 blade 1	-
Pratt & Whitney	-	PW2000 blade 1

In the hot corrosion environment, failure of TBCs with MCrAlY bond coat is primarily induced by cracking associated with the oxide scale formed as a result of hot corrosion attack of the bond coat material via the formation of nonuniform porous mixed oxide scales, instead of the degradation of the ceramic coating. This type of failure is independent of the microstructure and deposition chemistry of the ceramic coating<sup>131</sup>. The salt from engine intake and sulfur from fuels will react to form alkaline sulfates, depositing on turbine hardware, which could remain molten at the turbine operating temperatures<sup>132,133</sup>. The protective  $\text{Al}_2\text{O}_3$  layer, formed at the interface between the original ceramic coating and metallic bond coat, will dissolve in the alkaline sulfate melts<sup>134</sup>.



**Figure 7: Comparison of the cyclic oxidation kinetics of Pt-modified  $\beta$ -NiAl (50 at.% Al),  $\gamma'$ -Ni<sub>3</sub>Al +  $\gamma$ -Ni (22 at.% Al), and reactive-element (RE)-modified  $\gamma'$ -Ni<sub>3</sub>Al +  $\gamma$ -Ni (22 at.% Al) at 1150°C in air<sup>125</sup>.**

Ceramic matrix composites (CMCs) are promising candidates for applications in gas turbines, owing to their high temperature capabilities, high specific strength and lightweight. These characteristics offer substantial benefits in terms of engine performance (e.g. reduced requirement for cooling air), fuel savings and environmental concerns (e.g. reduced emission of CO<sub>x</sub> and NO<sub>x</sub>). However, in SiC-based CMCs, SiC will form a protective layer of SiO<sub>2</sub> upon heating, and will dissolve in the molten alkaline sulfate to form alkaline silicate<sup>135</sup>, which remains as a molten phase within the scale on the CMCs, making it easier for oxygen to diffuse through the molten scale to the SiC, and cause subsequent rapid reactions. In oxide-based CMCs, both SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> will dissolve in the molten alkaline sulfate<sup>134,135</sup>, leading to accelerated failure.

Therefore, thermal and environmental barrier coatings that are not susceptible to the deposition of alkaline sulfate and can act as a barrier to the diffusion of alkaline sulfate need to be developed to protect the superalloy and CMC substrates from hot corrosion during aircraft engine operation. Development of such thermal and environmental barrier coatings<sup>136</sup> is being undertaken by major engine and coating companies.

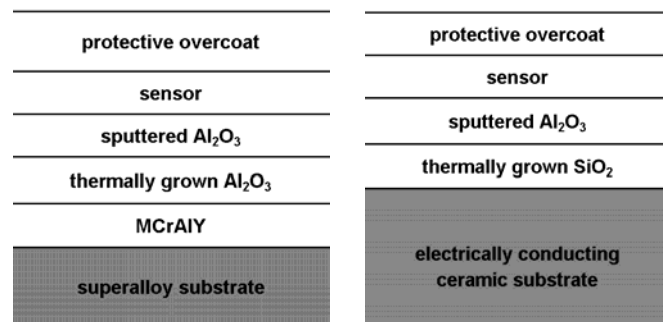
#### 4.0 EMBEDDED SENSORS

The cyclic nature and extreme values of stresses and temperatures in combustors and turbines, and the high value of their gradients, lead to a severe thermal and thermo-mechanical damage and short lives in engine hardware. To measure and model such damage accumulations require the use of reliable and non-intrusive sensors and work in this area is urgently needed.<sup>137</sup> Sensors that can provide both temperature and strain information will be an advantage for such an application.

Due to the application of protective coatings and advanced materials such as CMCs in aircraft engines, traditional wire strain gauges and thermocouples cannot be attached to the components via conventional spot-welding techniques. Sensors in a thin film form, embedded at the surface of the components, need to be developed to provide a minimally intrusive means of measuring surface parameters. These thin film sensors should have a thickness of only a few microns and thus add negligible mass to the surface, creating minimal disturbance of the gas flow over the surface and consequently minimal impact on the thermal, strain and vibration patterns that exist in the operating environment<sup>137</sup>.

The fabrication of thin film sensors could be performed in a clean room to minimize possible contamination. For an electrically conductive metal substrate, such as superalloy materials, a MCrAlY coating should be first deposited onto the substrate via a PVD process, followed by a heat treatment to form a stable, adherent and

electrically insulating alumina layer<sup>137</sup>. An additional layer of alumina could then be deposited onto the surface to fill any pinholes or cracks that may be present in the thermally grown alumina layer, since the thickness and electrical characteristics of the thermally grown alumina layer would not provide adequate high-temperature insulation between the sensor and the metal base<sup>138</sup>. Multilayered oxide/carbide insulating films should be better suited for insulation between thin film sensors and superalloy substrates in aircraft engines<sup>139</sup>. Electrically conductive ceramic materials, such as silicon carbide based CMCs, are thermally oxidized to form a stable, adherent silicon dioxide layer, and followed by another layer of PVD deposited alumina to obtain the insulation resistance. The sensors are fabricated onto the alumina layer, and then an alumina overcoat is deposited by PVD for protection, as shown in Figure 8.



**Figure 8: Schematic diagram of thin film sensors on superalloy and ceramic substrates<sup>137</sup>.**

NiCr and PdCr thin film strain gages were successfully deposited onto nickel-based superalloy substrates, and both showed good strain sensitivity at ambient temperatures<sup>140,141,142,143</sup>. Thin film NiCr strain gauges have been used successfully at 600°C in gas turbine engines and component rig dynamic strain testing; however, they may not be suitable for use at higher temperatures<sup>144</sup>. On the other hand, a thin film PdCr dynamic strain gauge showed a stable and repeatable apparent strain response up to 1100°C<sup>145</sup>, which is more suitable for both dynamic and static strain testing on superalloy, ceramic and CMC components of engines and aircraft structures<sup>144</sup>. Figure 9a shows a PdCr thin film dynamic strain gauge applied on a silicon nitride turbine blade. Indium tin oxide (ITO) thin films are being developed for high temperature applications, which are stable up to 1400°C<sup>146,147</sup>, and moreover, static strain testing indicated that the ITO thin film strain gages prepared with controlled nanoporosity survived repeated cyclic loading for tens of hours at temperatures up to 1581°C<sup>148</sup>.

A popular thin film thermocouple for engine applications may be PtRh/Pt thin films<sup>137,138,149,150,151</sup>, and studies showed these types of thermocouples to be accurate to 3% of the temperature gradient below 1200°C<sup>150</sup>. Figure 9b shows Pt13Rh/Pt thin film thermocouples applied on the space shuttle main engine turbine blade. However, PtRh/Pt thermocouples present some problems at high temperatures, such as substrate reaction, rhodium oxidation and film separation<sup>151,152,153</sup>. Other metallic thin film thermocouples for high temperature applications, such as Pt/Pd, were also explored, but the Pt/Pd thin film thermocouples yield stable output up to 850°C only<sup>154,155</sup>. Ceramic-based thermocouples are known for their high stability and robustness at high temperatures, but are typically found in the form of rods or probes<sup>156</sup>. Thin film ceramic-based thermocouples are still under development<sup>157,158</sup>.

In addition to its strain-gage application, the possibility of using an ITO thin film for a thermocouple application was also explored<sup>159</sup>, and the results showed a stable output of  $\pm 2\%$  for 10 hours at 575K.

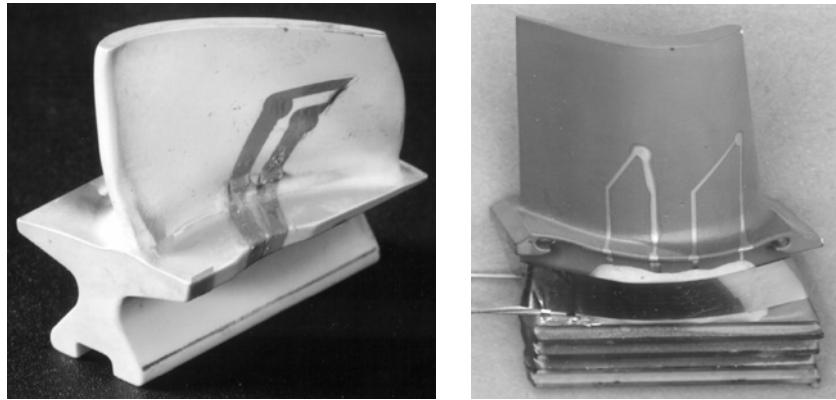


Figure 9: PdCr thin film dynamic strain gauge applied on a silicon nitride turbine blade (a) and Pt13Rh/Pt Thin film thermocouples applied on space shuttle main engine turbine blade (b)<sup>137</sup>.

## 5.0 STRUCTURE-POWER SYSTEMS

The application of electric-powered unmanned air vehicles (UAVs) and macro air vehicles (MAVs) offers significant help in both military and civilian missions. The vehicles are frequently powered by lithium or lithium-polymer batteries, which have high energy densities but relatively low power density<sup>160</sup>. The conventional stand-alone lithium-polymer batteries, however, are rather bulky and heavy for use in small UAVs, and therefore, thin-film batteries that can provide a rechargeable power source and can form the airfoil surfaces are of high interest in UAV and MAV applications<sup>161</sup>.

Recent developments have led to the use of rechargeable Telcordia plastic-lithium-ion (PLI) bicell batteries<sup>162</sup> sealed in a Dai-Nippon EI-40 packaging, which acts as a barrier-layer that is impermeable to moisture prior to acting with electrolyte<sup>163,164,165</sup>. The configurations of structure-battery systems<sup>166</sup> considered for UAVs and MAVs are shown in Figure 10.



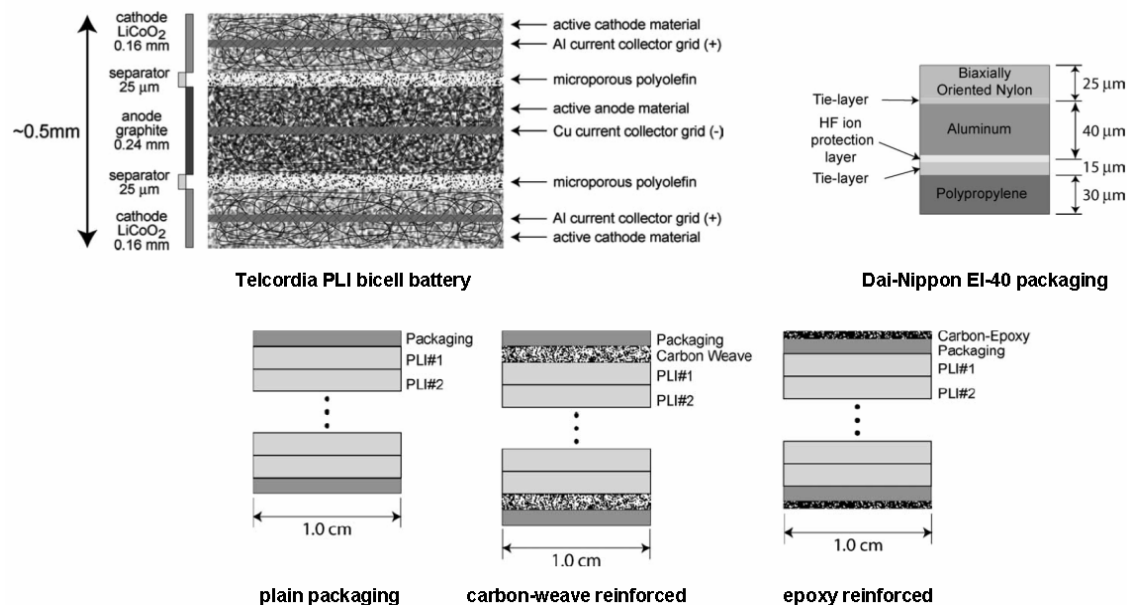


Figure 10: Telcordia PLI bicell battery, Dai-Nippon EI-40 packaging, and suggested structure-battery configurations<sup>166</sup>.

Another approach for structure-power systems involves the monopolar proton exchange membrane fuel cell, which can be shaped into a UAV airfoil skin. When applied to the skin, wings and antenna, the generated power levels could be sufficient to power the MAV. Also, by proper selection of materials, it can be sufficiently strong so that no additional reinforcement is required. Another feature of this multifunctional structure is the use of an integral metal grid for effective electromagnetic insulation and therefore, the structure can be used as an antenna, for communications or as part of a detector payload<sup>167</sup>. Figure 11 shows the MAVs powered by Telcordia PLI bicell battery and monopolar proton exchange membrane fuel cells. Other approaches include constant shape autophagous (self consuming) structure fuel, consuming solid fuel elements that provide structural stiffness until they are transformed or consumed for propulsion, and Variform - variable mass structure-power, utilizing inflatable wing structure that collapses in a prescribed manner to maintain aerodynamic function.

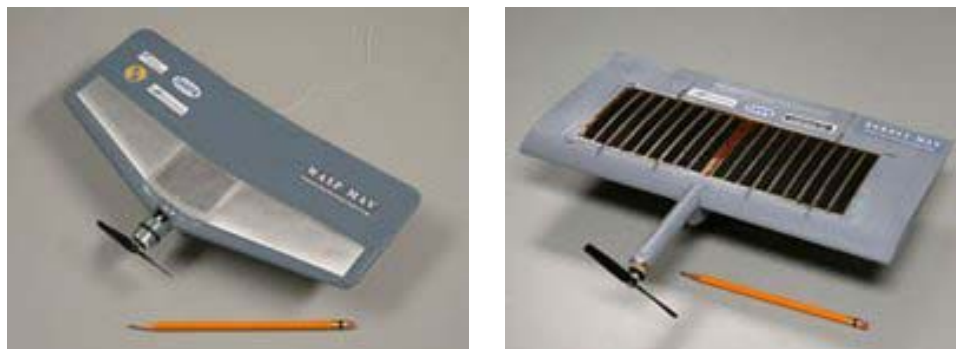


Figure 11 MAVs: Wasp powered by Telcordia PLI bicell batteries (a) and Hornet powered by monopolar proton exchange membrane fuel cells (b)<sup>167</sup>.



## 6.0 NANOTUBE COMPOSITES

The discovery of carbon nanotubes (CNTs)<sup>168</sup>, particularly the single-walled carbon nanotubes (SWCNTs)<sup>169,170</sup>, has attracted significant attention due to their exceptional mechanical properties<sup>171,172</sup> along with high thermal and electrical conductivities<sup>173,174</sup>. CNTs exist as either single-walled or multi-walled structures, and multi-walled carbon nanotubes (MWCNTs) are simply composed of concentric SWCNTs. The atomic structure of nanotubes is described in terms of the tube chirality, or helicity, which is defined by the chiral vector, also known as the roll-up vector,  $C_h$ , and chiral angle, illustrated as hexagonal graphite sheet<sup>175</sup> in Figure 12. Rolling the hexagonal graphite sheet in different ways leads to different types of nanotubes (Fig.13).

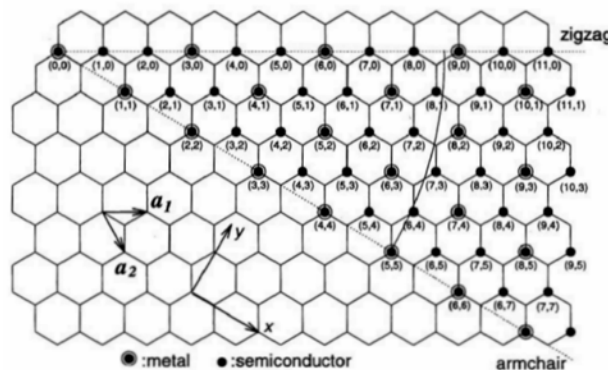


Figure 12: Schematic diagram showing how a nanotube can form via different rolling up<sup>175</sup>.

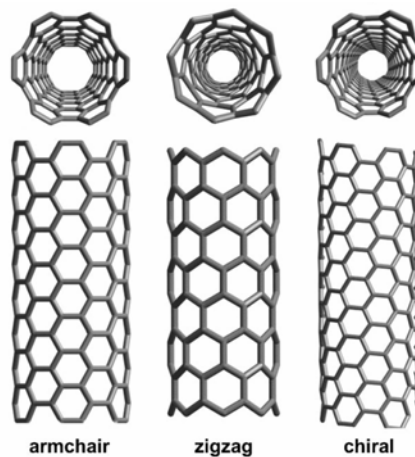


Figure 13: Molecular models of SWCNTs exhibiting different chiralities<sup>175</sup>.

Their ultra high strength (Table 3)<sup>176</sup>, along with their relatively low density, makes the CNTs, particularly in the form of CNT reinforced nanocomposites, an excellent candidate for aerospace structure applications<sup>177</sup>. CNT-based polymer composites exhibit improved strength, stiffness, and electrical conductivity<sup>178,179,180,181,182,183,184</sup>, etc. When embedded in ceramic matrix, CNTs may improve fracture

toughness and electrical conductivity of the ceramic<sup>185,186,187,188,189,190,191,192</sup>. In addition, it was shown that CNTs have higher lithium capacity<sup>193,194,195</sup>, compared with the theoretical value of graphite, exhibiting potential application as battery electrodes. It was suggested that alkali metals can be intercalated into the inter-shell spaces within the same MWCNT through defect sites<sup>196,197</sup>, or into the channels between SWCNTs and disrupt the intertube binding<sup>194</sup>. This makes CNTs potential candidates for structure-power applications.

While significant interests have been drawn to CNTs and their composites, some manufacturing issues still need to be addressed. CNTs are usually produced by electric arc-discharge<sup>169,170</sup>, laser vaporization<sup>198</sup> and CVD<sup>199</sup>, all of these methods use elements such as Fe, Co and Ni as catalyst. During fabrication, some metal particles, along with polyhedral graphite particles and amorphous carbon, will remain in the CNTs<sup>175</sup>. Therefore, purity and quality of the CNTs must be considered when making CNT reinforced composites, as remaining metal particles result in high density and possible interference of the metal and thermoset chemistries, whereas non-CNT carbon does not have the same reinforcing ability or conductivity<sup>177</sup>. Efforts to remove metal particles, polyhedral graphite particles and amorphous carbon have been extensive, and the purifying process may contain acid/hydrogen peroxide treatment and oxidation/vacuum heat treatment, probably with the assistance of filtration<sup>200,201,202,203,204,205,206,207,208,209,210</sup>.

**Table 3: Strength of carbon nanotubes**

	graphite crystal	carbon fibers	MWNT	SWNT	steel
tensile strength, GPa	100	3-7	300-600	300-1500	0.4
elastic modulus, GPa	1000	200-800	500-1000	1000-5000	200
specific strength, GPa	50	2-4	200-300	150-750	0.05
specific modulus, GPa	500	100-400	250-300	500-2500	26
strain to failure, %	10	1-3	20-40	20-40	25

The CNTs, usually grown as a tangled mass, need to be dispersed and aligned to achieve both structural and electrical/thermal transport properties of CNT reinforced polymer matrix composites. The alignment of the well dispersed CNTs can be achieved by hot pressing<sup>211</sup> and hot extrusion<sup>182</sup> and both showed improved mechanical properties and electrical conductivity compared with composites with randomly distributed CNTs. Figure 14 shows both as-grown CNTs and aligned CNTs in a polymer matrix. It is more difficult to align the CNTs within a ceramic matrix, since ceramics are more resistant to deformation. In addition, processing of the CNT reinforced ceramic matrix composites at high temperature with excessive time and/or pressure results in CNT damage<sup>212,213</sup>, leading to little or no enhancement of mechanical properties. A spark plasma sintering (SPS) technique that consolidates ceramic powders to near-theoretical density through the combined effects of rapid heating, pressure and powder surface cleaning, was thus introduced to the manufacture of CNT reinforced ceramic matrix composites<sup>187,188</sup>.

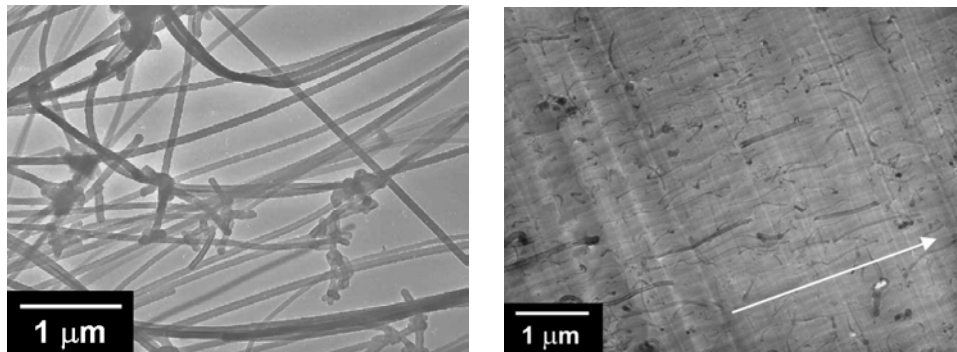


Figure 14: As-grown CNTs<sup>180</sup> (a) and aligned CNTs in a polymer matrix<sup>182</sup> (b).

SWCNTs also have a piezoresistive sensing property, an electrochemical actuation property, and a predictable, albeit very small, piezoelectric actuation property<sup>214</sup>. A SWCNT-epoxy composite layered actuator demonstrated response to a steady high voltage in a 2 M NaCl solution<sup>215</sup>, showing its potential to become a new smart material for structural applications. Other nanotubes, such as boron nitride (BN)<sup>216,217,218,219,220,221,222</sup>, boron-carbon-nitrogen (B-C-N)<sup>223,224,225,226,227</sup>, carbon-nitrogen (C-N)<sup>228</sup> and silicon carbide (SiC)<sup>229,230,231</sup>, were also produced. Among these materials boron nitride nanotubes (BNNTs) are believed to have exceptional thermal, electrical and mechanical properties, as well as chemical resistance<sup>214,232</sup>, and moreover, theoretical analyses showed that their characteristics offer the possibility of piezoelectric actuation tailored over a wide bandwidth, and the possibility of replacing piezoceramic materials with BNNTs.

## 7.0 CONCLUDING REMARKS

Materials that have a specific set of structural and functional properties, when used in aerospace vehicles, will lead to space and weight savings thus reducing the weight of aircraft. Such multifunctional materials are usually in the form of composites or multilayered coatings and therefore, material microstructure design for a specific set of structural and functional properties plays a very important role. Further development of multifunctional materials, the quality, cost and efficiency during manufacturing, as well as fundamental understanding of this type of materials deserve substantial attention.

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## SYMPOSIA DISCUSSION – PAPER NO: 14

**Author's Name: P.C. Patnaik**

**Question (H. Schippers):**

Can you explain the difference between multifunctional materials and multifunctional structures?

**Author's Response:**

The multifunctionality of structures can be achieved by means of:

- a) adaptive design of structures
- b) incorporating multifunctional materials.

Therefore one needs to incorporate multifunctional materials into multifunctional structures but not necessarily.

The multifunctionality can be introduced by innovative mechanical/structural design.

